

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-1-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **35** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** Sections – **A, B, C, D** and **E**.
- (iii) In **Section A** – Questions no. **1** to **18** are multiple choice (MCQ) type questions, carrying **1** mark each.
- (iv) In **Section B** – Questions no. **19** to **25** very short answer (VSA) type questions, carrying **2** marks each.
- (v) In **Section C** – Questions no. **26** to **30** are short answer (SA) type questions, carrying **3** marks each.
- (vi) In **Section D** – Questions no. **31** and **32** are case-based questions carrying **4** marks each.
- (vii) In **Section E** – Questions no. **33** to **35** are long answer (LA) type questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section B, 2 questions in Section C, 2 questions in Section D and 2 questions in Section E.
- (ix) Use of calculators is **not** allowed.

Section A (18 marks)

Questions no. 1 to 18 are Multiple Choice (MCQ) type Questions, carrying 1 mark each.

1. An α -helix is a structural feature of:

[1 mark]

- (A) Sucrose
- (B) Starch
- (C) Polypeptides
- (D) Nucleotides

Correct Answer: (C) Polypeptides

Solution:

Concept:

- Protein secondary structure describes the regular folding of a polypeptide backbone.
- An α -helix is stabilised by hydrogen bonds between backbone C = O and N – H groups.

Step 1: Identify the polymer A polypeptide consists of amino-acid residues joined through peptide bonds. Its backbone can coil into a regular right-handed helix, with hydrogen bonds maintaining the folded arrangement. Thus the alpha-helical feature belongs to protein secondary structure.

Step 2: Check the alternatives Sucrose is a disaccharide, while starch is a glucose polysaccharide; neither has a peptide backbone. Nucleotides are the units of nucleic acids. The double helix of DNA must not be confused with the α -helix of a polypeptide.

Step 3: Conclusion An α -helix is a structural feature of polypeptides. Hence, the correct option is (C).

Quick Tip to Solve: Look for a peptide backbone when the question mentions an alpha-helix; DNA has a double helix.

2. The glycosidic linkage involved in linking the glucose units in amylose part of starch is:

[1 mark]

- (A) $C_1 - C_6$ α linkage
- (B) $C_1 - C_6$ β linkage
- (C) $C_1 - C_4$ α linkage
- (D) $C_1 - C_4$ β linkage

Correct Answer: (C) $C_1 - C_4$ α linkage

Solution:

Concept:

- Amylose is the unbranched component of starch, built from α -D-glucose units.
- Its glycosidic bonds join carbon 1 of one glucose residue to carbon 4 of the next.

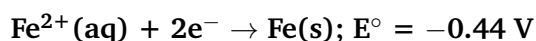
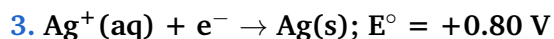
Step 1: Identify the starch component The unbranched glucose chain in starch is amylose. The wording refers to this starch component, whose repeated linkage is $\alpha(1 \rightarrow 4)$. Amylase is the enzyme that hydrolyses starch rather than a component of starch.

Quick Tip to Solve: For starch, pair amylose with alpha 1-to-4 and amylopectin branch points with alpha 1-to-6.

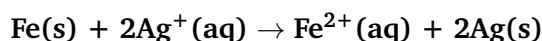
Step 2: Check the linkage choices The $C_1 - C_6$ α bond forms branch points in amylopectin, so (A) does not describe the linear amylose chain. The beta linkages in (B) and (D) are also unsuitable; the $\beta(1 \rightarrow 4)$ linkage is characteristic of cellulose.

Step 3: Conclusion The linkage is $C_1 - C_4$ α . Hence, the correct option is (C).

Quick Tip to Solve: For starch, pair amylose with alpha 1-to-4 and amylopectin branch points with alpha 1-to-6.



Find the E°_{cell} for:



[1 mark]

(A) 1.6 V

(B) -1.16 V

(C) 2.04 V

(D) 1.24 V

Correct Answer: (D) 1.24 V

Solution:

Concept:

- Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials.
- Electrode potential is an intensive quantity and is not multiplied by a stoichiometric coefficient.

Step 1: Identify the electrodes In the given reaction iron loses electrons and is oxidised at the anode, while silver ions gain electrons and are reduced at the cathode. Thus $E^\circ_{\text{cathode}} = +0.80 \text{ V}$ and the anode reduction potential is -0.44 V .

Step 2: Calculate the cell potential

$$E^\circ_{\text{cell}} = 0.80 - (-0.44) = 1.24 \text{ V}.$$

The coefficient 2 before silver does not double its potential. Option (C), 2.04 V, results from that incorrect operation; (A) and (B) do not equal the cathode-minus-anode difference.

Step 3: Conclusion $E^\circ_{\text{cell}} = 1.24 \text{ V}$. Hence, the correct option is (D).

Quick Tip to Solve: Keep both tabulated values as reduction potentials, subtract the anode value, and never multiply E by 2.

4. A first order reaction takes 30 minutes for 50% completion. The value of rate constant k would be: [1 mark]

- (A) $2.5 \times 10^{-3} \text{ min}^{-1}$
(B) $2.75 \times 10^{-4} \text{ min}^{-1}$
(C) $1.25 \times 10^{-3} \text{ min}^{-1}$
(D) $2.31 \times 10^{-3} \text{ min}^{-1}$

Correct Answer: $2.31 \times 10^{-2} \text{ min}^{-1}$; none of the printed options is correct.

Solution:

Concept:

- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$.
- Fifty per cent completion means the reactant concentration is half its initial value.

Step 1: Recognise the half-life The given time for 50% completion is exactly the half-life: $t_{1/2} = 30 \text{ min}$. There is no need to know the initial concentration because the half-life of a first-order reaction is independent of it.

Step 2: Calculate and compare every option

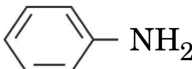
$$k = \frac{0.693}{30 \text{ min}} = 0.0231 \text{ min}^{-1} = 2.31 \times 10^{-2} \text{ min}^{-1}.$$

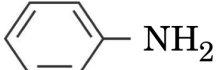
None of the printed values equals this result. Option (A) gives $2.5 \times 10^{-3} \text{ min}^{-1}$, whereas (B) gives $2.75 \times 10^{-4} \text{ min}^{-1}$. Option (C) gives $1.25 \times 10^{-3} \text{ min}^{-1}$, and (D) gives $2.31 \times 10^{-3} \text{ min}^{-1}$. In particular, (D) is smaller by a factor of ten.

Step 3: Conclusion $k = 2.31 \times 10^{-2} \text{ min}^{-1}$. None of the printed options is correct.

Quick Tip to Solve: For 50 per cent completion use $k = 0.693/t$ directly, and check the power of ten as well as the digits.

5. Which of the following is least basic? [1 mark]

- (A) $(\text{CH}_3)_2\text{NH}$ (B) NH_3
(C)  (D) $(\text{CH}_3)_3\text{N}$

Correct Answer: (C) 

Solution:

Concept:

- A base accepts a proton using the lone pair on nitrogen.
- Resonance delocalisation lowers lone-pair availability, while alkyl groups increase electron density through their inductive effect.

Quick Tip to Solve: Check whether nitrogen is directly attached to an aromatic ring: resonance then reduces its basicity.

Step 1: Examine aniline In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, the nitrogen lone pair is delocalised into the aromatic ring by resonance. It is therefore less available to bind a proton than the localised lone pair in ammonia or the listed aliphatic amines.

Step 2: Compare the alternatives Dimethylamine and trimethylamine have electron-releasing methyl groups, which favour proton acceptance relative to aniline. Ammonia has no aromatic ring into which its lone pair can delocalise. Although solvation affects the relative order of the aliphatic amines, it does not make either one less basic than aniline here.

Step 3: Conclusion Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is least basic. Hence, the correct option is (C).

Quick Tip to Solve: Check whether nitrogen is directly attached to an aromatic ring: resonance then reduces its basicity.

6. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives:

[1 mark]

(A) CH_3COONa

(B) CH_3NH_2

(C) $\text{CH}_3\text{CH}_2\text{Br}$

(D) $\text{CH}_3\text{CH}_2\text{NH}_2$

Correct Answer: (B) CH_3NH_2

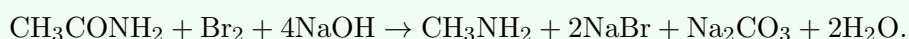
Solution:

Concept:

- Hofmann bromamide degradation converts RCONH_2 into RNH_2 using bromine and alkali.
- The product primary amine has one carbon atom fewer than the starting amide.

Step 1: Identify the transformation The reagents Br_2 and NaOH indicate Hofmann bromamide degradation. Acetamide is CH_3CONH_2 , so its group R is CH_3 ; the carbonyl carbon is removed during the rearrangement.

Step 2: Obtain the product and reject alternatives The balanced overall conversion is



Sodium acetate is a hydrolysis product, not the Hofmann product. Ethylamine retains two carbons, and bromoethane is not an amine, so (A), (D) and (C) are unsuitable.

Step 3: Conclusion The product is methylamine, CH_3NH_2 . Hence, the correct option is (B).

Quick Tip to Solve: Count carbons before choosing: Hofmann degradation changes a two-carbon amide into a one-carbon amine.

7. In the reaction $\text{R-OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{RCl} + \text{H}_2\text{O}$, what is the correct order of reactivity of alcohol?

[1 mark]

- (A) $1^\circ < 2^\circ < 3^\circ$
- (B) $1^\circ > 3^\circ > 2^\circ$
- (C) $1^\circ > 2^\circ > 3^\circ$
- (D) $3^\circ > 1^\circ > 2^\circ$

Correct Answer: (A) $1^\circ < 2^\circ < 3^\circ$

Solution:

Concept:

- Concentrated HCl and anhydrous ZnCl_2 form Lucas reagent, which converts alcohols into alkyl chlorides.
- For ordinary alkyl alcohols, reactivity follows carbocation stability: tertiary greater than secondary greater than primary.

Step 1: Explain the role of the reagent ZnCl_2 acts as a Lewis acid and helps the hydroxyl group leave. Tertiary alcohols react most rapidly because they readily produce relatively stable tertiary carbocations; secondary alcohols react more slowly, and primary alcohols are slowest under ordinary Lucas-test conditions.

Step 2: Match the printed order The increasing order is $1^\circ < 2^\circ < 3^\circ$. Option (A) states exactly this sequence. Options (B) and (C) place primary alcohols above tertiary ones, while (D) incorrectly places primary above secondary. All three conflict with the normal Lucas-reagent reactivity trend.

Step 3: Conclusion The correct order is $1^\circ < 2^\circ < 3^\circ$. Hence, the correct option is (A).

Quick Tip to Solve: With HCl/ ZnCl_2 , put tertiary alcohol first in decreasing reactivity, then secondary, then primary.

8. The colligative property used for the determination of molar mass of polymers and proteins is:

[1 mark]

- (A) Osmotic pressure
- (B) Depression in freezing point
- (C) Relative lowering in vapour pressure
- (D) Elevation in boiling point

Correct Answer: (A) Osmotic pressure

Solution:

Concept:

- Osmotic pressure is a colligative property: for a dilute solution, $\pi V = nRT$.
- If mass w of a solute of molar mass M is dissolved in volume V , then $M = wRT/(\pi V)$.

Step 1: Compare the measurable effects Polymers and proteins have very high molar masses, so even an appreciable mass gives a small number of solute particles. Their freezing-point depression,

Quick Tip to Solve: For a very large molar mass, choose osmotic pressure: it is measurable in dilute solutions at room temperature.

boiling-point elevation and relative lowering of vapour pressure are therefore very small and difficult to measure accurately.

Step 2: Choose the suitable method Osmotic pressure remains sufficiently large to measure in very dilute solutions. It can also be measured at room temperature, avoiding the heating that can denature proteins. Thus option (A) is suitable; options (B), (C) and (D) give less accurately measurable changes for such macromolecules.

Step 3: Conclusion Osmotic pressure is used. Hence, the correct option is (A).

Quick Tip to Solve: For a very large molar mass, choose osmotic pressure: it is measurable in dilute solutions at room temperature.

9. Low concentration of oxygen in the blood and tissues of people living at high altitude is due to: [1 mark]

- (A) high atmospheric pressure
- (B) low temperature
- (C) low atmospheric pressure
- (D) low temperature and high atmospheric pressure both

Correct Answer: (C) low atmospheric pressure

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the partial pressure of the gas and x its mole fraction in solution.
- At a fixed temperature, a lower gas partial pressure gives a lower dissolved concentration.

Step 1: Identify the pressure change Atmospheric pressure decreases with increasing altitude. Although the fraction of oxygen in air remains approximately the same, its partial pressure decreases because the total atmospheric pressure is lower.

Step 2: Apply Henry's law and eliminate alternatives At lower oxygen partial pressure, less oxygen dissolves in blood, so the oxygen supplied to tissues decreases. High atmospheric pressure, as in (A), would favour increased gas solubility. Low temperature in (B) is not the stated cause and generally favours gas dissolution; (D) also incorrectly includes high pressure.

Step 3: Conclusion The cause is low atmospheric pressure. Hence, the correct option is (C).

Quick Tip to Solve: Use oxygen partial pressure, rather than oxygen percentage, to connect altitude with gas solubility.

10. Which of the following is affected by catalyst?

[1 mark]

- (A) ΔH
- (B) ΔG
- (C) E_a
- (D) ΔS

Correct Answer: (C) E_a

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy E_a .
- Thermodynamic changes ΔH , ΔG and ΔS depend on the initial and final states.

Step 1: Identify the kinetic effect Activation energy is the energy barrier that reacting particles must overcome. A catalyst changes the pathway and lowers this barrier, increasing the reaction rate at the same temperature. In the Arrhenius expression $k = Ae^{-E_a/(RT)}$, a smaller barrier favours a larger rate constant.

Step 2: Check the other choices The reactants and products remain the same when a catalyst is used. Their enthalpy, Gibbs energy and entropy differences therefore remain unchanged: options (A), (B) and (D) are not affected. A catalyst speeds up approach to equilibrium but does not change the equilibrium constant.

Step 3: Conclusion Activation energy E_a is affected. Hence, the correct option is (C).

Quick Tip to Solve: Separate pathway properties from state functions: a catalyst changes the barrier, not reactant-to-product energy differences.

11. The compounds $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ and $[\text{Co}(\text{Br})(\text{NH}_3)_5]\text{SO}_4$ represent:

[1 mark]

- (A) optical isomerism
- (B) linkage isomerism
- (C) ionisation isomerism
- (D) coordination isomerism

Correct Answer: (C) ionisation isomerism

Solution:

Concept:

- Ionisation isomers exchange a ligand inside the coordination sphere with a counter-ion outside it.
- Such complexes have the same overall composition but produce different ions in solution.

Step 1: Locate the exchanged groups In $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$, sulfate is coordinated and bromide lies outside the square brackets. In $[\text{Co}(\text{Br})(\text{NH}_3)_5]\text{SO}_4$, bromide is coordinated and sulfate is the counter-ion.

Step 2: Classify and distinguish the alternatives The first complex releases bromide counter-ions in water, whereas the second releases sulfate counter-ions. This interchange establishes ionisation

Quick Tip to Solve: Compare the species inside and outside the square brackets: counter-ion and ligand exchange signals ionisation isomerism.

isomerism. It is not optical isomerism (mirror-image arrangements), linkage isomerism (different donor atoms of one ligand), or coordination isomerism (ligand exchange between complex cations and complex anions).

Step 3: Conclusion The compounds exhibit ionisation isomerism. Hence, the correct option is (C).

Quick Tip to Solve: Compare the species inside and outside the square brackets: counter-ion and ligand exchange signals ionisation isomerism.

12. The synthesis of alkyl fluoride is best obtained from:

[1 mark]

- (A) Free radicals
- (B) Swartz reaction
- (C) Sandmeyer reaction
- (D) Finkelstein reaction

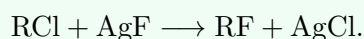
Correct Answer: (B) Swartz reaction

Solution:

Concept:

- The Swarts reaction prepares alkyl fluorides by replacing chlorine or bromine with fluorine.
- Metallic fluorides such as AgF or SbF_3 supply fluoride in this halogen-exchange reaction.

Step 1: Recall the preparation An alkyl chloride or bromide is treated with an appropriate metallic fluoride. A representative equation is



This is the Swarts reaction (spelt Swartz in the option).

Step 2: Check the alternatives Free-radical halogenation is not the preferred controlled route to alkyl fluorides. The Sandmeyer reaction concerns replacement of a diazonium group in aromatic compounds, rather than the required alkyl-halide exchange. The Finkelstein reaction uses sodium iodide to prepare alkyl iodides, not fluorides. Thus only option (B) matches the desired product.

Step 3: Conclusion The synthesis is best obtained by the Swarts reaction. Hence, the correct option is (B).

Quick Tip to Solve: Remember the exchanged halogen: Swarts gives alkyl fluoride; Finkelstein gives alkyl iodide.

13. The most common and stable oxidation state of a Lanthanoid is:

[1 mark]

- (A) +2
- (B) +3
- (C) +4
- (D) +6

Correct Answer: (B) +3

Solution:

Concept:

- The characteristic and most common oxidation state of lanthanoids is +3.
- Lanthanoids generally lose two 6s electrons and one additional 5d or 4f electron to form Ln^{3+} .

Step 1: Identify the usual electron loss The outer electron configuration of lanthanoids generally involves 4f, 5d and 6s orbitals. Removal of the two outer 6s electrons and one further electron gives the trivalent ion. This oxidation state occurs throughout the series and is the standard stable state in their compounds.

Step 2: Distinguish exceptional states Some members can also exhibit +2 or +4 where particularly favourable empty, half-filled or filled 4f arrangements result. These are exceptions and are not the most common state of the whole series. The +6 choice is not the characteristic lanthanoid state. Therefore (A), (C) and (D) do not answer the question.

Step 3: Conclusion The most common and stable oxidation state is +3. Hence, the correct option is (B).

Quick Tip to Solve: For the lanthanoid series as a whole, select +3; treat +2 and +4 as element-specific exceptions.

14. The order of the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{h\nu} 2\text{HCl}(\text{g})$ is:

[1 mark]

- (A) 2
- (B) 1
- (C) 0
- (D) 3

Correct Answer: (C) 0

Solution:

Concept:

- Reaction order is determined from the experimental rate law, not the balanced chemical equation.
- The photochemical combination of hydrogen and chlorine is treated as a zero-order reaction under fixed illumination.

Step 1: Use the photochemical condition The symbol $h\nu$ over the arrow shows that light initiates the reaction. Under the fixed illumination conditions of this standard photochemical example, the rate is governed by the incident light rather than by the concentrations of hydrogen and chlorine. The rate

Quick Tip to Solve: The light symbol identifies the standard photochemical example; do not add equation coefficients to obtain order.

law is therefore represented as $r = k$.

Step 2: Determine the order and reject coefficient counting Equivalently, $r = k[\text{H}_2]^0[\text{Cl}_2]^0$, so the sum of concentration exponents is $0 + 0 = 0$. Adding the reactant stoichiometric coefficients would give 2, but that does not determine an experimental reaction order. Neither order 1 nor order 3 follows from this zero-order rate law.

Step 3: Conclusion The reaction is zero order. Hence, the correct option is (C).

Quick Tip to Solve: The light symbol identifies the standard photochemical example; do not add equation coefficients to obtain order.

15. Assertion (A): $(\text{C}_2\text{H}_5)_2\text{NH}$ is more basic than $(\text{C}_2\text{H}_5)_3\text{N}$ in aqueous solution.

Reason (R): In $(\text{C}_2\text{H}_5)_2\text{NH}$, there is more steric hindrance and +I effect than $(\text{C}_2\text{H}_5)_3\text{N}$.

Select the correct answer:

[1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- In water, amine basicity depends on electron donation, steric hindrance and hydration of the conjugate acid.
- The +I effect of an ethyl group increases electron density on nitrogen; hydration stabilises the protonated amine.

Step 1: Judge the assertion Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, is more basic than triethylamine in aqueous solution. Its conjugate acid is better hydrated, and nitrogen is less crowded. These effects outweigh the greater electron donation of three ethyl groups. Thus A is true.

Step 2: Judge the reason Triethylamine has three ethyl groups, whereas diethylamine has two. Therefore the tertiary amine has greater steric hindrance and a greater cumulative +I effect. R reverses both comparisons and is false.

Step 3: Check the explanation and codes A false reason cannot explain a true assertion. Codes (A) and (B) require R to be true, and code (D) requires A to be false, so all three are rejected.

Step 4: Conclusion Assertion is true and Reason is false. Hence, the correct option is (C).

Quick Tip to Solve: For aqueous basicity, compare hydration and crowding as well as the number of alkyl groups.

16. Assertion (A): The molecularity of the reaction $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$ appears to be 2.

Reason (R): Two molecules of the reactants are involved in the given elementary reaction.

Select the correct answer:

[1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept:

- Molecularity of an elementary reaction is the number of reacting species taking part in one elementary event.
- For an elementary equation, count reactant molecules using their stoichiometric coefficients.

Step 1: Judge the assertion The written equation is $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$. On the elementary-reaction interpretation explicitly used in R, one hydrogen molecule and one bromine molecule participate. The apparent molecularity is therefore $1 + 1 = 2$, so A is true.

Step 2: Judge the reason R states that two reactant molecules participate in the given elementary reaction. This is exactly the molecule count in the written equation, so R is true. Molecularity counts reactants, not the two product molecules.

Step 3: Check the explanatory link The presence of two reacting molecules directly explains the apparent molecularity of two. Thus (B), which denies this link, and (C) and (D), which declare one statement false, are rejected. The overall hydrogen-bromine reaction can have a multistep mechanism; molecularity strictly belongs to an elementary step, consistent with the word "appears" in A.

Step 4: Conclusion Both statements are true on the stated elementary-reaction interpretation, and R explains A. Hence, the correct option is (A).

Quick Tip to Solve: Count molecules on the reactant side of an elementary step; do not infer molecularity from products.

17. Assertion (A): Acetylation of aniline gives a monosubstituted product.

Reason (R): Activating effect of $-\text{NHCOCH}_3$ group is more than that of amino group.

Select the correct answer:

[1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (A) is false, but Reason (R) is true.

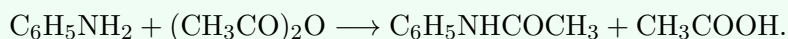
Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Acetylation converts aniline into acetanilide, replacing one amino hydrogen with an acetyl group.
- The $-\text{NHCOCH}_3$ group activates the benzene ring less strongly than $-\text{NH}_2$, because the nitrogen lone pair also conjugates with the carbonyl group.

Step 1: Judge the assertion Aniline undergoes acetylation to form the monoacetylated product acetanilide:



Protection by acetylation also moderates subsequent ring substitution, allowing a monosubstituted ring product under suitable conditions. Thus A is true.

Step 2: Judge the reason In acetanilide the nitrogen lone pair is shared with the carbonyl group as well as the aromatic ring. Its availability for donating electron density to the ring is reduced. Therefore $-\text{NHCOCH}_3$ is less activating than the amino group, not more; R is false.

Step 3: Check the explanatory link The reduced activating effect is the relevant chemical explanation. The opposite comparison in R cannot explain A. Options (A) and (B) require a true R, while (D) requires a false A, and are rejected.

Step 4: Conclusion Assertion is true and Reason is false. Hence, the correct option is (C).

Quick Tip to Solve: Acetyl protection shares the nitrogen lone pair with a carbonyl, reducing activation of the ring.

18. Assertion (A): EDTA is used to determine hardness of water.

Reason (R): EDTA is a bidentate ligand.

Select the correct answer:

[1 mark]

- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Hardness of water is principally due to dissolved Ca^{2+} and Mg^{2+} ions.
- EDTA is a hexadentate ligand, coordinating through two nitrogen and four carboxylate oxygen donor atoms.

Step 1: Judge the assertion EDTA forms stable complexes with calcium and magnesium ions. In a complexometric titration it binds a metal ion in a 1 : 1 molar ratio, allowing the concentration of hardness-producing ions to be determined from the amount of EDTA consumed. Thus A is true.

Step 2: Judge the reason EDTA can bind through six donor atoms: two nitrogen atoms and one oxygen atom from each of four carboxylate groups. It is therefore hexadentate, not bidentate, so R is false.

Step 3: Check the explanation and options The stable chelate formation accounts for its use in hardness determination, but the incorrect denticity stated in R cannot explain A. Options (A) and (B) require R to be true, and option (D) requires A to be false.

Step 4: Conclusion Assertion is true and Reason is false. Hence, the correct option is (C).

Quick Tip to Solve: Remember EDTA donor count as two nitrogen atoms plus four oxygen atoms, giving six donor sites.

Section B (14 marks)

19. A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute.

(Vapour pressure of pure water at 308 K = 32 mm Hg)

[2 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile solute, Raoult's law gives $(p^0 - p)/p^0 \simeq n_2/n_1$.
- Here $n_1 = w_1/M_1$ for water and $n_2 = w_2/M_2$ for solute; water has molar mass $M_1 = 18 \text{ g mol}^{-1}$.

Quick Tip to Solve: Compute the dimensionless relative lowering first; keep the solvent mass in the denominator.

Step 1: Calculate the relative lowering The non-volatile solute lowers the water vapour pressure. Using both pressures in the same unit,

$$\frac{p^0 - p}{p^0} = \frac{32 - 31.84}{32} = \frac{0.16}{32} = 0.005.$$

The temperature is already the same for the solution and pure solvent, so no temperature conversion is required.

Step 2: Substitute the masses Using the standard dilute-solution expression,

$$0.005 = \frac{w_2 M_1}{w_1 M_2} = \frac{10 \times 18}{200 M_2}.$$

Hence

$$M_2 = \frac{10 \times 18}{200 \times 0.005} = 1800 \text{ g mol}^{-1}.$$

The small relative lowering justifies replacing solvent mole fraction denominator by solvent moles. For comparison, using the exact relation $0.005 = n_2/(n_1 + n_2)$ gives $M_2 = 1791 \text{ g mol}^{-1}$, a difference of only 0.5%. The dilute value is the usual board-level result.

Step 3: Conclusion The molar mass of the solute is 1800 g mol^{-1} using the dilute-solution approximation.

Quick Tip to Solve: Compute the dimensionless relative lowering first; keep the solvent mass in the denominator.

20. Explain briefly:

(a) Carbylamine reaction

(b) Gabriel phthalimide synthesis

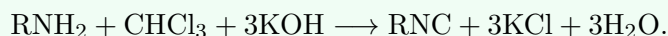
[2 marks]

Solution:

Concept:

- Primary amines give the carbylamine reaction with chloroform and alcoholic potassium hydroxide.
- Gabriel synthesis uses alkylation of potassium phthalimide followed by hydrolysis to prepare primary aliphatic amines.

Step 1: Explain the carbylamine reaction On heating a primary aliphatic or aromatic amine with chloroform and alcoholic KOH, a foul-smelling isocyanide (carbylamine) is formed:



The conditions are alcoholic KOH and heating. Secondary and tertiary amines do not give this test, so it is used to identify primary amines. In RNC, the organic group is bonded to nitrogen; the product is an isocyanide, not a nitrile.

Step 2: Explain Gabriel phthalimide synthesis Phthalimide is treated with alcoholic KOH to obtain potassium phthalimide. Its nitrogen anion reacts with a primary alkyl halide RX by nucleophilic sub-

Quick Tip to Solve: Use carbylamine as the primary-amine test; Gabriel synthesis requires an alkyl halide, not an aryl halide.

stitution to give N-alkylphthalimide. Hydrolysis of this intermediate releases RNH_2 and phthalic acid (or phthalate under alkaline conditions). This route gives a primary aliphatic amine without further alkylation to secondary or tertiary amines. Aryl halides do not undergo the required substitution readily, so the method is unsuitable for preparing aniline.

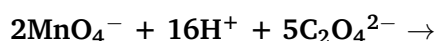
Step 3: Conclusion (a) Carbylamine reaction forms isocyanides from primary amines. (b) Gabriel synthesis prepares primary aliphatic amines through N-alkylphthalimide and hydrolysis.

Quick Tip to Solve: Use carbylamine as the primary-amine test; Gabriel synthesis requires an alkyl halide, not an aryl halide.

21. How would you account for:

(a) The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ couple or $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

(b) Complete the following equation:



[2 marks]

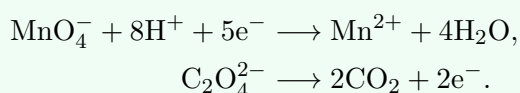
Solution:

Concept:

- Reduction potential measures the tendency of M^{3+} to accept an electron and form M^{2+} . A more positive value favours this reduction.
- A half-filled $3d^5$ subshell is especially stable; redox equations conserve atoms and total charge.

Step 1: Explain the relative reduction potentials Mn^{3+} has configuration $3d^4$, whereas Mn^{2+} is $3d^5$. Reduction produces the particularly stable half-filled configuration, so it is strongly favourable. In contrast, Cr^{3+} has stable $3d^3$ configuration and reduction gives Cr^{2+} , $3d^4$. Also, Fe^{3+} is already half-filled $3d^5$, while Fe^{2+} is $3d^6$; its reduction loses that special stability. These differences account for the much more positive manganese potential.

Step 2: Balance the acidic redox reaction The reduction and oxidation half-reactions are



Multiply the first by two and the second by five to cancel ten electrons. The products are two manganese(II) ions, ten carbon dioxide molecules and eight water molecules. Both sides contain two Mn atoms, ten C atoms and twenty-eight O atoms; total charge is +4 on each side.

Step 3: Conclusion Mn^{2+} is stabilised by its half-filled $3d^5$ configuration. The completed equation is



Quick Tip to Solve: Compare the d-electron configurations before and after reduction; balance acidic permanganate using five electrons per Mn.

22(a). On diluting two electrolytes 'A' and 'B', the Λ_m of 'A' increases 25 times while that of 'B' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically. [2 marks]

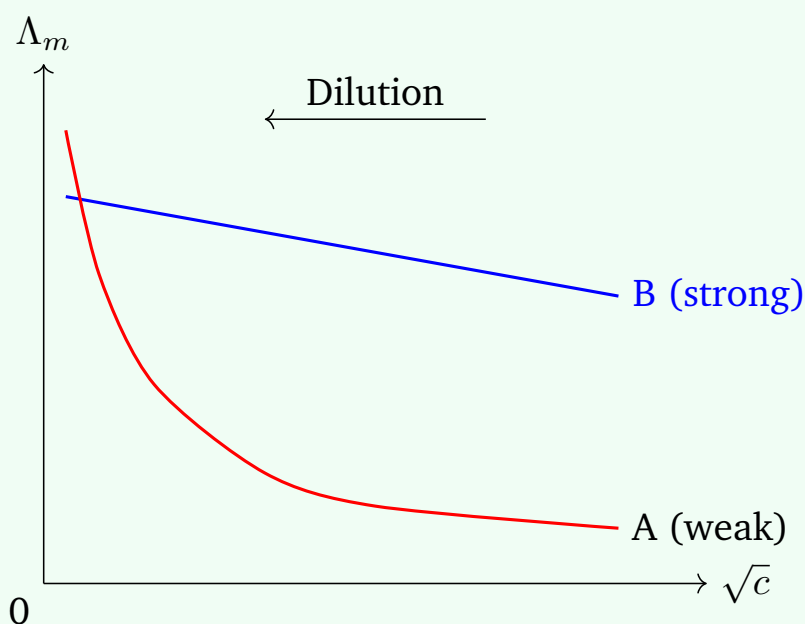
Solution:

Concept:

- Molar conductivity $\Lambda_m = \kappa/c$ expresses conductance per mole, with consistent concentration units.
- Strong electrolytes are almost completely ionised; weak electrolytes become much more ionised on dilution.

Step 1: Identify the strong electrolyte For B, dilution increases Λ_m by only a factor of 1.5. Its ions are already substantially present, so dilution mainly reduces interionic interactions and increases their mobility. A rises by a factor of 25, indicating a large increase in the number of ions from further dissociation. Thus the modest change identifies B as strong and the much larger change identifies A as weak.

Step 2: Justify with conductivity curves Plot Λ_m against $\sqrt{c}$, where c is concentration. For a strong electrolyte, $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$, with $K > 0$, is approximately a straight line at low concentration. Its conductivity rises gently as dilution moves the point left. For a weak electrolyte, the curve rises steeply towards the dilute limit because its degree of ionisation increases. The schematic curves below show these distinct shapes; their absolute vertical positions are illustrative, since the question gives ratios rather than absolute conductivities.



Schematic molar conductivity curves; dilution is towards the left.

Step 3: Conclusion Electrolyte **B** is strong; A is weak. B shows a small, approximately linear increase on dilution, while A shows a much larger curved increase.

Quick Tip to Solve: On a conductivity-versus-square-root-concentration graph, dilution means moving left towards zero concentration.

22(b). The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate the conductivity. [2 marks]

Solution:

Concept:

- Conductivity is $\kappa = G(l/A) = l/(RA)$, where R is resistance, $G = 1/R$ is conductance, l is length and A is cross-sectional area.
- For a cylindrical solution column, $A = \pi r^2$, with radius $r = d/2$.

Step 1: Calculate the cell constant The diameter is $d = 1 \text{ cm}$, so the radius is 0.5 cm , not 1 cm . Hence

$$A = \pi(0.5)^2 = 0.7854 \text{ cm}^2.$$

With $l = 50 \text{ cm}$, the cell constant is

$$\frac{l}{A} = \frac{50}{0.7854} = 63.66 \text{ cm}^{-1}.$$

Using centimetres throughout gives conductivity in siemens per centimetre.

Step 2: Use resistance to obtain conductivity The measured resistance is $R = 5.55 \times 10^3 \Omega$, so

$$G = \frac{1}{R} = 1.8018 \times 10^{-4} \text{ S}.$$

Therefore

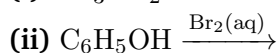
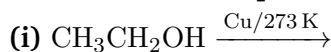
$$\kappa = G \frac{l}{A} = (1.8018 \times 10^{-4})(63.66) = 1.147 \times 10^{-2} \text{ S cm}^{-1}.$$

The stated concentration is not needed for this calculation: resistance and cell dimensions directly determine conductivity. Concentration would be required to calculate molar conductivity instead. Since $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$, the equivalent SI value is 1.147 S m^{-1} .

Step 3: Conclusion The conductivity is $\boxed{\kappa \approx 1.15 \times 10^{-2} \text{ S cm}^{-1}}$, or 1.15 S m^{-1} .

Quick Tip to Solve: Halve the diameter before computing area, and keep all cell dimensions in the same length unit.

23(a). Predict the products of the following reactions:



[2 marks]

Solution:

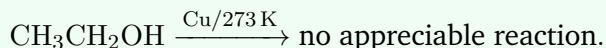
Concept:

- Copper catalyses dehydrogenation of a primary alcohol to the corresponding aldehyde: two hydrogen atoms are removed without changing its carbon skeleton.

Quick Tip to Solve: Check temperature as well as reagent: ethanol dehydrogenation requires heated copper; bromine water gives three substitutions on phenol.

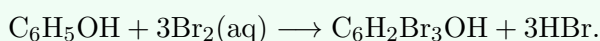
- The hydroxyl group activates the phenol ring and directs electrophilic substitution to its ortho and para positions.

Step 1: Predict the product from ethanol The official reaction arrow specifies copper at 273 K. This is not the heated-copper condition needed for the usual dehydrogenation of a primary alcohol. At the printed temperature, no appreciable reaction is expected and ethanol remains unchanged:



For comparison, passing ethanol vapour over heated copper at 573 K produces ethanal by loss of hydrogen, $\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2$. That different-temperature reaction does not give the literal answer to the printed 273 K condition. Thus no aldehyde formation is assigned under the condition actually stated.

Step 2: Predict the product from aqueous bromine Phenol reacts readily with bromine water because its hydroxyl group strongly activates the aromatic ring. Bromine substitutes at both ortho positions (2 and 6) and the para position (4), forming 2,4,6-tribromophenol as a white precipitate:



The bromine water is decolourised. Aqueous bromine gives the trisubstituted product, rather than only a monobromophenol.

Step 3: Conclusion (i) At the printed Cu/273 K condition, no appreciable reaction occurs; ethanol remains unchanged. (ii) 2,4,6-Tribromophenol, $\text{C}_6\text{H}_2\text{Br}_3\text{OH}$, is formed as a white precipitate.

Quick Tip to Solve: Check temperature as well as reagent: ethanol dehydrogenation requires heated copper; bromine water gives three substitutions on phenol.

OR

23(b). Give reasons for the following:

(i) p-nitrophenol is more acidic than p-methylphenol.

(ii) $(\text{CH}_3)_3\text{C}-\text{Br}$ on reaction with NaOCH_3 gives alkene as the main product and not an ether. [2 marks]

Solution:

Concept:

- A phenol is more acidic when its conjugate base, the phenoxide ion, is more stable; electron-withdrawing groups stabilise its negative charge.
- A tertiary haloalkane resists $\text{S}_{\text{N}}2$ attack because of steric hindrance. A strong base can instead remove a β -hydrogen by elimination.

Step 1: (i) Compare phenoxide-ion stability The para nitro group withdraws electrons by both inductive and resonance effects. It stabilises the negative charge of the p-nitrophenoxide ion, favouring loss of H^+ . The para methyl group donates electrons through its positive inductive effect and makes the p-methylphenoxide ion less stable. Thus the nitro-substituted phenol releases its proton more

Quick Tip to Solve: Compare conjugate-base stability for acidity; with a tertiary halide and a strong alkoxide base, look for beta-elimination.

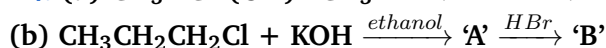
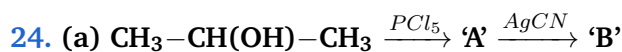
readily.

Step 2: (ii) Explain elimination The carbon bearing bromine in $(CH_3)_3CBr$ is tertiary and crowded, so backside attack required for ether formation by S_N2 is hindered. Methoxide is a strong base: it abstracts a hydrogen from an adjacent methyl group while bromide leaves, producing 2-methylpropene by beta-elimination.



Step 3: Conclusion (i) p-Nitrophenol is more acidic because its conjugate base is stabilised by the nitro group. (ii) Steric hindrance suppresses substitution, so the main product is 2-methylpropene.

Quick Tip to Solve: Compare conjugate-base stability for acidity; with a tertiary halide and a strong alkoxide base, look for beta-elimination.



Identify 'A' and 'B' in the above reactions.

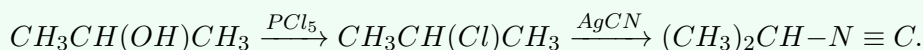
[2 marks]

Solution:

Concept:

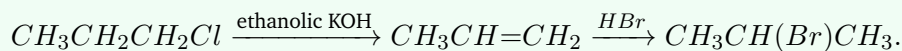
- PCl_5 replaces the hydroxyl group of an alcohol by chlorine. Silver cyanide is predominantly covalent and reacts through nitrogen to give an isocyanide, $R-NC$.
- Alcoholic KOH promotes beta-elimination. Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov's rule.

Step 1: (a) Replace hydroxyl, then form the isocyanide Propan-2-ol first forms 2-chloropropane. Reaction with AgCN gives isopropyl isocyanide, with the alkyl group bonded to nitrogen:



Thus A is 2-chloropropane and B is isopropyl isocyanide. AgCN must be distinguished from KCN, which generally gives the nitrile through carbon.

Step 2: (b) Eliminate HCl, then add HBr Ethanolic KOH removes a beta-hydrogen and chlorine from adjacent carbons of 1-chloropropane, giving propene. In HBr addition, hydrogen adds to the terminal carbon and bromine to the middle carbon:



No peroxide is specified, so the anti-Markovnikov product is not selected.

Step 3: Conclusion (a) $A = CH_3CH(Cl)CH_3$; $B = (CH_3)_2CH-N \equiv C$. (b) $A = CH_3CH=CH_2$; $B = CH_3CH(Br)CH_3$.

Quick Tip to Solve: Use AgCN to identify an isocyanide; alcoholic KOH gives an alkene, and ordinary HBr addition places Br on the more substituted carbon.

25. Define denaturation of protein. What is the effect of denaturation on the structure of protein?

[2 marks]

Solution:

Concept:

- Protein function depends on the specific three-dimensional folding of its polypeptide chains, maintained by hydrogen bonding and other stabilising interactions.
- The primary structure is the amino-acid sequence joined by peptide bonds; secondary and tertiary structures describe folding and spatial arrangement.

Step 1: Define denaturation Denaturation is the process in which a protein loses its native structure and biological activity under the action of heat, a change in pH, or suitable chemical agents. Such conditions disrupt the interactions responsible for its characteristic folded shape. For example, the coagulation of egg white on heating illustrates protein denaturation.

Step 2: State the structural effect During denaturation, the regular secondary structure and the tertiary structure are disrupted, and the polypeptide unfolds. If a protein has several subunits, their association may also be affected. The peptide bonds are not hydrolysed in ordinary denaturation, so the primary structure, namely the sequence of amino acids, remains unchanged. Loss of the native shape explains the loss of biological activity.

Step 3: Conclusion Denaturation destroys the native folding and biological activity of a protein. Its secondary and tertiary structures are disrupted, while its primary structure remains intact.

Quick Tip to Solve: Distinguish unfolding from peptide-bond hydrolysis: denaturation changes folding, whereas hydrolysis breaks the amino-acid chain.

Section C (15 marks)

26. Give reason:

- (a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers.
- (b) Aquatic animals are more comfortable in cold water than in warm water.
- (c) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution.

[3 marks]

Solution:

Concept:

- Osmotic pressure obeys $\pi = CRT = wRT/(MV)$, where C is molar concentration, w is solute mass, M its molar mass and V solution volume.
- Gas solubility generally increases on cooling. Colligative properties depend on the number of solute particles; boiling-point elevation is $\Delta T_b = iK_b m$.

Step 1: (a) Choose a sensitive method at room temperature Proteins and polymers have very large molar masses, so even an appreciable mass gives a small molar concentration. Their boiling-

Quick Tip to Solve: For macromolecules choose osmotic pressure; for dissolved gases track temperature; for colligative properties count independent particles.

point elevation or freezing-point depression is therefore extremely small and difficult to measure accurately. Osmotic pressure is appreciable even for very dilute solutions and can be measured at room temperature, avoiding thermal decomposition or denaturation of sensitive macromolecules. The measured value gives $M = wRT/(\pi V)$.

Step 2: (b) Relate temperature to dissolved oxygen Oxygen dissolves more readily in cold water than in warm water. Dissolution of gases is generally exothermic, so cooling favours the dissolved state. In Henry's law, $p = K_H x$, the Henry constant increases with temperature; at a given oxygen pressure, the dissolved mole fraction x therefore decreases on warming. Cold water supplies more dissolved oxygen for respiration, making aquatic animals more comfortable.

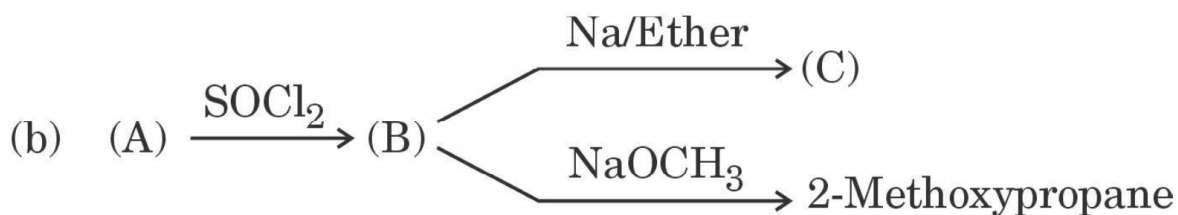
Step 3: (c) Count particles in the two solutions KCl dissociates into K^+ and Cl^- , yielding nearly two particles per formula unit, so its van't Hoff factor is approximately 2. Sugar is a non-electrolyte and remains as molecules, with $i = 1$. Hence $\Delta T_b = iK_b m$ gives nearly twice the elevation for KCl at comparable concentration. The printed comparison uses equal molarity; for dilute aqueous solutions the corresponding molalities are approximately equal. Non-ideal ionic behaviour explains why the increase is nearly, rather than exactly, double.

Step 4: Conclusion (a) Osmotic pressure is measurable in dilute solutions at room temperature. (b) Cold water contains more dissolved oxygen. (c) KCl produces nearly twice as many solute particles as sugar.

Quick Tip to Solve: For macromolecules choose osmotic pressure; for dissolved gases track temperature; for colligative properties count independent particles.

27. Complete the following reactions:

[3 marks]



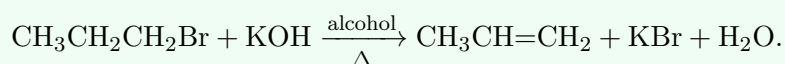
Solution:

Concept:

- Alcoholic KOH with heat causes beta-elimination of HBr from a haloalkane, giving an alkene.
- HBr adds to propene according to Markovnikov's rule when peroxide is absent. Thionyl chloride replaces an alcohol's OH group by chlorine.
- Wurtz coupling joins two alkyl groups using sodium in dry ether. An alkoxide can replace halide to form an ether.

Quick Tip to Solve: In part (b), work backwards from the ether: remove the methoxy group to identify the carbon bearing halogen in B.

Step 1: Part (a): form the alkene Heating 1-bromopropane with alcoholic KOH removes a hydrogen from the adjacent carbon and bromine from the terminal carbon:



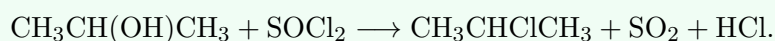
Thus the intermediate (A) in part (a) is propene. Alcoholic conditions favour elimination; aqueous KOH would instead favour substitution.

Step 2: Part (a): add hydrogen bromide In the absence of peroxide, H adds to the terminal carbon of propene and Br to its middle carbon:

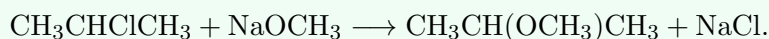


This gives (B), 2-bromopropane, through the more stable secondary carbocation.

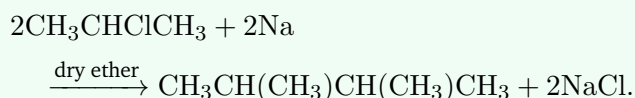
Step 3: Part (b): identify the alcohol and chloride The letters in part (b) denote a separate reaction sequence. The ether product has a propan-2-yl group attached to oxygen. Hence (B) is 2-chloropropane and its alcohol precursor (A) is propan-2-ol:



Reaction with sodium methoxide gives the specified ether:



Step 4: Part (b): identify the coupling product Sodium in dry ether couples two propan-2-yl groups at the carbons that bore chlorine:



The coupled carbon skeleton has six carbons; choosing its longest chain gives a butane chain with methyl groups at positions 2 and 3.

Step 5: Conclusion (a) (A) = propene; (B) = 2-bromopropane. (b) (A) = propan-2-ol; (B) = 2-chloropropane; (C) = 2,3-dimethylbutane.

Quick Tip to Solve: In part (b), work backwards from the ether: remove the methoxy group to identify the carbon bearing halogen in B.

28. How do you convert the following: (Any three)

(a) Phenol to 2-Hydroxybenzaldehyde

(b) Anisole to 2-Methoxyacetophenone

(c) Propene to Propan-2-ol

(d) Ethanol to Ethanal

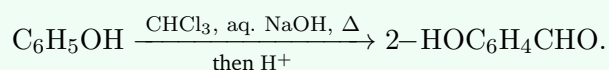
[3 marks]

Solution:

Concept:

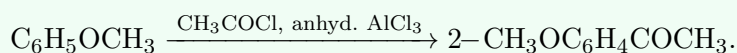
- Reimer-Tiemann formylation introduces a CHO group mainly ortho to the hydroxyl group of phenol.
- Anisole undergoes Friedel-Crafts acylation at ortho and para positions because its methoxy group activates the ring.
- Acid-catalysed hydration of an alkene follows Markovnikov's rule; controlled oxidation or catalytic dehydrogenation converts a primary alcohol to an aldehyde.

Step 1: (a) Phenol to 2-hydroxybenzaldehyde Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. This is the Reimer-Tiemann reaction. The intermediate is hydrolysed to give the aldehyde group mainly at the ortho position:



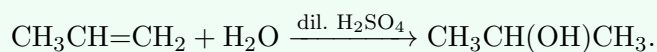
The product is salicylaldehyde (2-hydroxybenzaldehyde); the phenolic OH remains on the ring.

Step 2: (b) Anisole to 2-methoxyacetophenone Treat anisole with acetyl chloride in the presence of anhydrous aluminium chloride. Friedel-Crafts acylation introduces the acetyl group, -COCH_3 , on the aromatic ring:



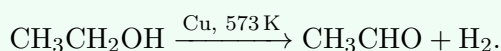
Both ortho and para products form; isolate the ortho isomer to obtain the requested 2-methoxyacetophenone. The para isomer is usually the major product, so the desired ortho product should not be described as the sole product.

Step 3: (c) Propene to propan-2-ol Hydrate propene with water in the presence of dilute sulphuric acid:



Hydrogen adds to the terminal carbon, while OH appears on the middle carbon. This Markovnikov addition therefore gives the secondary alcohol propan-2-ol.

Step 4: (d) Ethanol to ethanal Pass ethanol vapour over heated copper at 573 K. The primary alcohol undergoes dehydrogenation:



Removing two hydrogen atoms creates the carbonyl group while retaining the two-carbon skeleton. This method directly gives ethanal without using an oxidant that may further oxidise it to ethanoic

Quick Tip to Solve: Keep each carbon skeleton unchanged and match the reagent to the new group: CHO by Reimer-Tiemann, acetyl by acylation, and OH by hydration.

acid.

Step 5: Conclusion Use (a) $\text{CHCl}_3/\text{NaOH}$, heat and acidification; (b) $\text{CH}_3\text{COCl}/\text{AlCl}_3$, followed by separation of the ortho isomer; (c) acid-catalysed hydration; (d) Cu at 573 K. Any three conversions may be written.

Quick Tip to Solve: Keep each carbon skeleton unchanged and match the reagent to the new group: CHO by Reimer-Tiemann, acetyl by acylation, and OH by hydration.

29. (a) What are the hydrolysis products of (i) Lactose, (ii) Maltose?

(b) Give the basic structural difference between starch and cellulose.

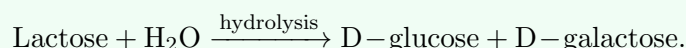
[3 marks]

Solution:

Concept:

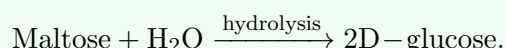
- Hydrolysis breaks a glycosidic bond by addition of water, releasing the constituent monosaccharides of a disaccharide.
- The alpha and beta configurations of glucose determine the glycosidic linkages and the shape of glucose polysaccharide chains.

Step 1: (a)(i) Hydrolysis of lactose Lactose is composed of one D-galactose unit and one D-glucose unit joined by a beta-(1 to 4) glycosidic linkage. Hydrolysis cleaves this linkage and gives one molecule of each monosaccharide:



Thus lactose does not give two glucose molecules; its galactose component distinguishes it from maltose.

Step 2: (a)(ii) Hydrolysis of maltose Maltose contains two D-glucose units connected by an alpha-(1 to 4) glycosidic linkage. Breaking the linkage by hydrolysis releases both glucose units:



Both lactose and maltose are disaccharides, so each consumes one water molecule when its single inter-unit glycosidic bond is hydrolysed.

Step 3: (b) Structural difference between starch and cellulose Starch is built from alpha-D-glucose units. Its amylose component has alpha-(1 to 4) linkages and forms an unbranched, helical chain. Amylopectin has alpha-(1 to 4) linkages along the chains and alpha-(1 to 6) linkages at branching points. Cellulose is built from beta-D-glucose units connected by beta-(1 to 4) glycosidic linkages. Its chains are straight and unbranched, with neighbouring glucose units oppositely oriented. Hydrogen bonding between these chains contributes to a rigid fibrous structure. Hence the basic difference is the alpha glucose linkages in starch versus the beta glucose linkages in cellulose, rather than a difference in their monosaccharide identity or general polysaccharide formula.

Step 4: Conclusion Lactose gives D-glucose and D-galactose; maltose gives two D-glucose molecules. Starch contains alpha-D-glucose linkages, whereas cellulose contains beta-D-glucose units linked by

Quick Tip to Solve: Remember lactose as glucose plus galactose, maltose as glucose plus glucose, and compare starch with cellulose by alpha versus beta linkages.

beta-(1 to 4) bonds.

Quick Tip to Solve: Remember lactose as glucose plus galactose, maltose as glucose plus glucose, and compare starch with cellulose by alpha versus beta linkages.

30(a). Explain why:

(i) Carboxyl group in benzoic acid is meta directing.

(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.

(iii) Carboxylic acids do not give characteristic reactions of carbonyl group.

[3 marks]

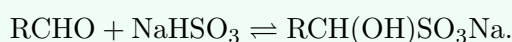
Solution:

Concept:

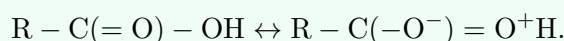
- The carboxyl group withdraws electron density by both the inductive effect ($-I$) and the resonance effect ($-M$).
- Nucleophilic addition depends on the electrophilicity of the carbonyl carbon; resonance and reversible addition account for the stated behaviour.

Step 1: (i) Meta-directing carboxyl group In benzoic acid, $-\text{COOH}$ withdraws electrons from the ring. Resonance particularly reduces electron density at the ortho and para positions. In electrophilic substitution at either of these positions, the intermediate has an especially unfavourable resonance contributor with positive charge at the carbon bearing the electron-withdrawing group. The meta intermediate avoids this contributor. Thus, although the ring is deactivated overall, substitution is favoured at the meta position.

Step 2: (ii) Purification through a bisulphite addition compound Aldehydes and suitable ketones react with sodium bisulphite to form crystalline addition compounds. These crystals can be separated from impurities by filtration and washed. Treatment with dilute acid or alkali decomposes the addition compound and regenerates the pure carbonyl compound. For an aldehyde, the reversible addition is



Step 3: (iii) Resonance reduces carbonyl electrophilicity In a carboxylic acid, a lone pair on the hydroxyl oxygen is delocalised towards the carbonyl group:



This electron donation reduces the positive character of the carbonyl carbon. Consequently, carboxylic acids do not undergo the characteristic nucleophilic addition reactions of aldehydes and ketones; they generally undergo reactions involving replacement of the hydroxyl group instead.

Step 4: Conclusion The explanations are: electron withdrawal favours meta substitution; reversible crystalline bisulphite addition enables purification; and resonance lowers the electrophilicity of the carboxyl carbon.

Quick Tip to Solve: For a carboxyl group, connect ring substitution to electron withdrawal and carbonyl reactivity to donation from its hydroxyl oxygen.

30(b). An organic compound 'A', having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives 'B'. 'B' does not reduce Fehling's solution but gives a yellow precipitate of the compound 'C' with $I_2/NaOH$. Deduce the structures of A, B and C. [3 marks]

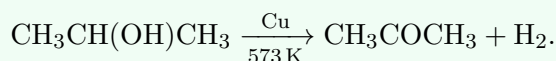
Solution:

Concept:

- An alcohol vapour passed over heated copper at 573 K undergoes dehydrogenation: a primary alcohol gives an aldehyde and a secondary alcohol gives a ketone.
- Methyl ketones contain CH_3CO- and give a yellow precipitate of iodoform, CHI_3 , with $I_2/NaOH$.

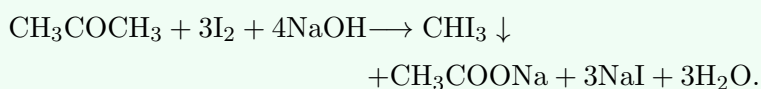
Step 1: Identify the carbonyl compound B The molecular formula C_3H_8O permits propan-1-ol, propan-2-ol and an ether. Copper dehydrogenation to a carbonyl compound identifies A as an alcohol. Propan-1-ol would give propanal, which reduces Fehling's solution. Since B does not reduce this solution, B is the ketone propanone, CH_3COCH_3 . Its methyl ketone groups also explain the positive iodoform test.

Step 2: Obtain A from dehydrogenation The secondary alcohol that gives propanone is propan-2-ol. Its hydroxyl-bearing carbon is bonded to two methyl groups. Removal of hydrogen from the O-H bond and from this carbon forms the carbonyl bond:



Thus the alcohol has exactly the required formula C_3H_8O .

Step 3: Identify the yellow precipitate C Propanone undergoes the haloform reaction. The balanced equation is



The yellow precipitate is iodoform, with one carbon atom bonded to one hydrogen and three iodine atoms. Sodium ethanoate is the soluble organic product, not the yellow precipitate.

Step 4: Conclusion $A = CH_3CH(OH)CH_3$, $B = CH_3COCH_3$, $C = CHI_3$. A is propan-2-ol, B is propanone and C is iodoform.

Quick Tip to Solve: A negative Fehling test plus a positive iodoform test identifies the three-carbon carbonyl product as propanone.

Section D (8 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

31(i). If $\text{PtCl}_2 \cdot 2\text{NH}_3$ does not react with AgNO_3 , what will be its formula?

[1 mark]

Solution:

Concept:

- Silver nitrate detects ionisable chloride ions outside the coordination sphere through precipitation of AgCl .
- Ligands inside square brackets belong to the coordination sphere and do not give this test as free chloride ions.

Step 1: Locate the chloride ions No reaction with AgNO_3 means there is no ionisable chloride outside the coordination sphere. Hence both chloride groups in $\text{PtCl}_2 \cdot 2\text{NH}_3$ must be coordinated directly to platinum.

Step 2: Place all ligands inside the sphere The two neutral ammonia ligands also coordinate to platinum. With platinum in oxidation state +2 and two coordinated chloride ligands each of charge -1, the complex is neutral. No chloride counterion is required outside the brackets.

Step 3: Conclusion The formula is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Quick Tip to Solve: If silver nitrate gives no AgCl , place every chloride ligand inside the coordination brackets.

31(ii). What is the secondary valency of $[\text{Co}(\text{en})_3]^{3+}$?

[1 mark]

Solution:

Concept:

- Werner's secondary valency is the coordination number: the number of donor atoms directly bonded to the central metal.
- Ethylenediamine, en, is a neutral bidentate ligand; each molecule coordinates through two nitrogen donor atoms.

Step 1: Count donors from each ligand In $[\text{Co}(\text{en})_3]^{3+}$, three ethylenediamine molecules surround cobalt. Each ligand has two nitrogen atoms with lone pairs available for coordination, and both nitrogen atoms bind to the metal.

Step 2: Calculate the coordination number The total number of metal-donor bonds is $3 \times 2 = 6$. The superscript $3+$ is the charge of the complex, not its secondary valency; similarly, the subscript 3 counts ligand molecules rather than donor atoms.

Step 3: Conclusion The secondary valency of cobalt is 6 .

Quick Tip to Solve: For bidentate en, double the number of ligand molecules to obtain the secondary valency.

31(iii). (1) Write the formula of Iron(III)hexacyanidoferrate(II).

(2) Write the IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

[2 marks]

Solution:

Concept:

- In a neutral coordination salt, the total positive and negative charges balance. Each cyanido ligand, CN^- , has charge -1 .
- Name ligands alphabetically before the central metal; neutral NH_3 is ammine and coordinated Cl^- is chlorido. The metal oxidation state is written in Roman numerals.

Step 1: Determine the ions and their ratio For hexacyanidoferrate(II), the central iron has oxidation state $+2$. Six cyanido ligands contribute -6 , so the complex ion is $[\text{Fe}(\text{CN})_6]^{4-}$. Iron(III) outside the coordination sphere is Fe^{3+} . The least common multiple of 3 and 4 is 12, hence four iron(III) ions balance three complex anions: $4(+3) + 3(-4) = 0$.

Step 2: Name the cobalt salt In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, the two outer chloride ions require a complex charge of $+2$. If cobalt has oxidation state x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The five ammine ligands precede chlorido alphabetically; the counter-ion is named chloride.

Step 3: Conclusion (1) The formula is $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

(2) The IUPAC name is pentaamminechloridocobalt(III) chloride.

Quick Tip to Solve: Balance ionic charges first; distinguish chlorido inside brackets from chloride outside them.

OR

31(iii). Write the hybridization and magnetic behaviour of $[\text{Ni}(\text{CN})_4]^{2-}$. [Atomic number: $\text{Ni} = 28$]

[2 marks]

Solution:

Concept:

- The oxidation state of the metal follows from ligand charges and the charge on the complex. Cyanido, CN^- , is a strong-field ligand.
- In valence bond theory, one available inner d orbital, one s and two p orbitals produce dsp^2 hybridisation and square-planar geometry. A species without unpaired electrons is diamagnetic.

Step 1: Find the electronic configuration of nickel(II) Let the oxidation state of nickel in $[\text{Ni}(\text{CN})_4]^{2-}$ be x . Then $x + 4(-1) = -2$, so $x = +2$. Nickel, with atomic number 28, has configuration $[\text{Ar}]3d^84s^2$; removal of the two $4s$ electrons gives $\text{Ni}^{2+} : [\text{Ar}]3d^8$.

Step 2: Account for pairing and bonding The strong-field cyanido ligands cause the eight $3d$ electrons to pair in four orbitals, leaving one inner $3d$ orbital vacant. That vacant orbital combines with the $4s$ and two $4p$ orbitals to form four dsp^2 hybrid orbitals. These accept ligand lone pairs in a square-planar arrangement. All the metal electrons are paired, so there is no permanent magnetic moment from unpaired electrons.

Quick Tip to Solve: For nickel(II), first identify the ligand strength: cyanido pairs the d electrons and gives square-planar bonding.

Step 3: Conclusion dsp^2 hybridisation; diamagnetic. The complex is square planar and has zero unpaired electrons.

Quick Tip to Solve: For nickel(II), first identify the ligand strength: cyanido pairs the d electrons and gives square-planar bonding.

32(i). Case Study: The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation.

(i) What is average rate of reaction?

[1 mark]

Solution:

Concept:

- Average rate measures the change in concentration over a finite time interval $\Delta t = t_2 - t_1$.
- Reactant concentration decreases, so a minus sign makes its consumption rate positive; product concentration increases.

Step 1: Choose the concentration change For a reactant R , write $\Delta[R] = [R]_2 - [R]_1$. Since $[R]_2 < [R]_1$, this change is negative. For a product P , the corresponding change $\Delta[P]$ is positive.

Step 2: Divide by elapsed time For a reaction $R \rightarrow P$ with unit stoichiometric coefficients, the average rate is

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}.$$

For other stoichiometric coefficients, divide each expression by its respective coefficient to define the common reaction rate.

Step 3: Conclusion Average rate of reaction is the decrease in reactant concentration or increase in product concentration per unit time over a specified finite time interval.

Quick Tip to Solve: Use a finite concentration difference for average rate and retain the minus sign for a reactant.

32(ii). Write two factors that affect the rate of reaction.

[1 mark]

Solution:

Concept:

- Reaction rate depends on the frequency of effective collisions between reacting particles.
- An effective collision requires sufficient energy to overcome the activation-energy barrier and suitable orientation.

Step 1: Consider reactant concentration Increasing reactant concentration generally places more

Quick Tip to Solve: Name concentration and temperature, then connect them to collision frequency and the fraction of energetic particles.

reacting particles in a given volume, increasing collision frequency. Thus concentration can affect the rate according to the reaction's rate law; its precise dependence is set by the experimentally determined order.

Step 2: Consider temperature At a higher temperature, particles have a higher average kinetic energy and a larger fraction can overcome the activation-energy barrier. The rate constant generally increases, so the reaction becomes faster under otherwise identical conditions.

Step 3: Conclusion Two factors affecting the rate of reaction are **reactant concentration and temperature**.

Quick Tip to Solve: Name concentration and temperature, then connect them to collision frequency and the fraction of energetic particles.

32(iii). (1) What happens to rate of reaction for zero order reaction?

(2) What is the unit of k for zero order reaction?

[2 marks]

Solution:

Concept:

- For a zero-order reaction involving reactant A , the rate law is $r = k[A]^0$, where k is the rate constant.
- Rate has dimensions of concentration divided by time. The unit of a rate constant follows by substituting the reaction order into its rate law.

Step 1: Determine how concentration affects the rate For nonzero reactant concentration in the range where the zero-order law applies, $[A]^0 = 1$. Therefore

$$r = k[A]^0 = k.$$

The rate is independent of reactant concentration. At fixed temperature and other reaction conditions, changing the concentration does not alter this rate; it remains constant while the zero-order behaviour persists.

Step 2: Derive the unit of the rate constant Because $r = k$, the rate constant has the same unit as reaction rate. Concentration is commonly measured in mol L^{-1} and time in seconds. Thus

$$[k] = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{-1} \text{s}^{-1}.$$

Equivalently this unit is M s^{-1} , where M denotes molarity.

Step 3: Conclusion (1) The rate is constant and independent of reactant concentration: $r = k$. (2) The unit of k is $\boxed{\text{mol L}^{-1} \text{s}^{-1}}$.

Quick Tip to Solve: Set the concentration exponent to zero before deriving units; the zero-order rate constant has the units of rate itself.

32(iii). (1) For a reaction $P + 2Q \rightarrow \text{Products}$, $\text{Rate} = k[P]^{1/2}[Q]^1$. What is the order of the reaction?
 (2) Define pseudo first order reaction with an example. [2 marks]

Solution:

Concept:

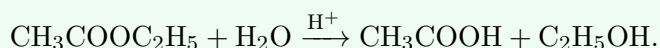
- Reaction order is the sum of powers of reactant concentrations in the experimental rate law, not the sum of stoichiometric coefficients.
- In a pseudo first order reaction, an excess reactant has effectively constant concentration, so the observed rate depends on the first power of only one reactant.

Step 1: (1) Calculate the overall order In $r = k[P]^{1/2}[Q]^1$, the orders with respect to P and Q are $1/2$ and 1 , respectively. Therefore,

$$n = \frac{1}{2} + 1 = \frac{3}{2}.$$

The coefficient 2 of Q in the reaction equation is not its order. The experimentally specified concentration exponent is the authority for this calculation.

Step 2: (2) Define and illustrate pseudo first order kinetics A pseudo first order reaction has actual order greater than one but follows first order kinetics when another reactant is present in large excess and its concentration remains practically constant. An example is acid-catalysed hydrolysis of ethyl acetate in excess water:



At fixed acid concentration, $r = k[\text{ester}][\text{H}_2\text{O}]$. Since water is in large excess, its consumption scarcely changes its concentration. Thus $k' = k[\text{H}_2\text{O}]$ is effectively constant and the observed law is $r = k'[\text{ester}]$. This apparent first order behaviour arises from the experimental conditions.

Step 3: Conclusion (1) The order is $\boxed{3/2}$. (2) A reaction of higher actual order that behaves as first order because another reactant is in large excess is pseudo first order, as in ethyl acetate hydrolysis in excess water.

Quick Tip to Solve: Add rate-law powers for order; identify the excess reactant whose concentration is absorbed into the effective rate constant.

Section E (15 marks)

33. Assign reason for each of the following:

- (i) Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements.
- (ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.
- (iii) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidising agent.
- (iv) Zn has lowest enthalpy of atomization.
- (v) Cu^+ is unstable in an aqueous solution.

[5 marks]

Solution:

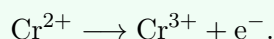
Concept:

- Transition-metal oxidation states depend on the participation of both outer ns and $(n-1)d$ electrons; stable electronic arrangements influence redox behaviour.
- Variable oxidation states, intermediate formation and adsorption on metal surfaces help transition metals act as catalysts.
- Metallic bonding determines atomization enthalpy, while hydration of ions contributes to their stability in aqueous solution.

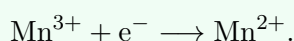
Step 1: (i) Highest oxidation state of manganese Manganese has electronic configuration $[\text{Ar}]3d^54s^2$. It possesses seven valence electrons: five in $3d$ and two in $4s$. All seven can participate in bonding with highly electronegative elements such as oxygen, allowing the oxidation state +7, for example in MnO_4^- . This is the highest oxidation state exhibited in the 3d series.

Step 2: (ii) Catalytic activity of transition metals Transition metals can adopt several oxidation states and readily form complexes or intermediate compounds with reactants. These intermediates provide an alternative reaction pathway with lower activation energy, and the catalyst is regenerated. In heterogeneous catalysis, their surfaces also adsorb reactants, bringing them together and weakening bonds before reaction. These properties explain the catalytic activity of many transition metals and their compounds.

Step 3: (iii) Opposite redox tendencies of two d-four ions Although both ions initially have d^4 configurations, their accessible products have different stabilizing features. Cr^{2+} readily loses an electron:



The resulting Cr^{3+} has the stable d^3 configuration, with a favourable t_{2g}^3 arrangement in an octahedral field. Hence Cr^{2+} reduces another species and acts as a reducing agent. In contrast,



Mn^{2+} has a stable half-filled $3d^5$ configuration. Consequently, Mn^{3+} accepts an electron and oxidises another species, acting as an oxidising agent.

Step 4: (iv) Low atomization enthalpy of zinc Zinc has configuration $[\text{Ar}]3d^{10}4s^2$, with a completely

Quick Tip to Solve: For redox reasons, write the ion's electron change and identify the stable product; in aqueous copper chemistry, include hydration rather than relying only on d-shell filling.

filled 3d subshell and no unpaired d electrons. Its filled d shell contributes little to the strong metallic bonding found in many other 3d metals. Zinc therefore has relatively weak metallic bonding, so less energy is needed to separate its solid into gaseous atoms. This explains its lowest atomization enthalpy in the series.

Step 5: (v) Instability of copper(I) in water In aqueous solution, Cu^+ undergoes disproportionation:



One copper(I) ion is oxidised to copper(II) and another is reduced to copper metal. The more negative hydration enthalpy of Cu^{2+} , owing to its higher charge density, provides sufficient stabilization to compensate for the energy required to oxidise Cu^+ . Thus the products are favoured despite the filled d^{10} configuration of Cu^+ .

Step 6: Conclusion The reasons are: (i) participation of seven Mn valence electrons; (ii) variable oxidation states, intermediate formation and adsorption; (iii) formation of stable Cr^{3+} and half-filled Mn^{2+} ; (iv) weak Zn metallic bonding with a filled d shell; and (v) hydration-driven disproportionation of Cu^+ .

Quick Tip to Solve: For redox reasons, write the ion's electron change and identify the stable product; in aqueous copper chemistry, include hydration rather than relying only on d-shell filling.

34(a). (i) Carry out the following conversions:

(1) Ethanal to But-2-en-1-al

(2) Propanoic acid to 2-chloropropanoic acid

(ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms iodoform. Identify the compounds 'A', 'B' and 'C'.

[5 marks]

Solution:

Concept:

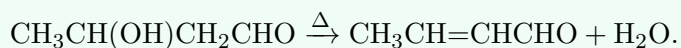
- Aldehydes having an α -hydrogen undergo aldol addition with dilute alkali; heating the aldol eliminates water to give an α, β -unsaturated aldehyde.
- The Hell-Volhard-Zelinsky reaction replaces an α -hydrogen of a carboxylic acid by halogen using halogen and red phosphorus, followed by hydrolysis.
- Reductive ozonolysis breaks an alkene's double bond into two carbonyl groups. Fehling's test identifies an aliphatic aldehyde, while the iodoform test identifies the $\text{CH}_3\text{CO}-$ group, including ethanal.

Step 1: (i)(1) Convert ethanal by aldol condensation Ethanal has an α -hydrogen. Two ethanal molecules first combine in dilute sodium hydroxide to give 3-hydroxybutanal (the aldol):



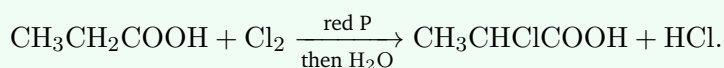
Quick Tip to Solve: Identify the aldehyde from the intersection of Fehling and iodoform tests first; then use the five-carbon total to fix the ketone before reconnecting the carbonyl carbons.

On heating, the aldol loses water from its hydroxyl group and an adjacent hydrogen. The resulting double bond is conjugated with the aldehyde group:



Numbering from the aldehyde carbon places the double bond between C-2 and C-3; this product is but-2-en-1-al (crotonaldehyde).

Step 2: (i) (2) Chlorinate propanoic acid at the alpha carbon Apply the Hell–Volhard–Zelinsky reaction using chlorine in the presence of red phosphorus, followed by hydrolysis:



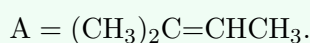
The carbon adjacent to the carboxyl carbon is C-2. Replacement of one of its hydrogens by chlorine therefore gives 2-chloropropanoic acid. This reaction introduces chlorine at the required position while retaining the carboxylic acid group.

Step 3: (ii) Identify B using both positive tests A positive Fehling's test means B is an aliphatic aldehyde. Among such aldehydes, ethanal alone gives the iodoform test because it contains the required $\text{CH}_3\text{CO}-$ arrangement, with hydrogen attached to the carbonyl carbon. Thus $\text{B} = \text{CH}_3\text{CHO}$, ethanal. Its iodoform reaction is

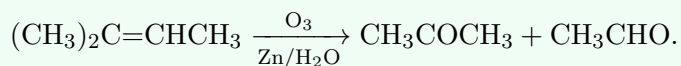


The yellow precipitate of CHI_3 confirms the inference. An aldehyde such as propanal would give Fehling's test but would fail the iodoform test.

Step 4: Identify C and reconstruct the alkene A Ozonolysis conserves the number of carbon atoms. Since A has five carbon atoms and B has two, C must have three. C fails Fehling's test but gives iodoform, so it is a methyl ketone: $\text{C} = \text{CH}_3\text{COCH}_3$, propanone (acetone). Replace the oxygen of each carbonyl product by a bond joining its carbonyl carbon to the other. The ethanal carbon retains CH_3 and H, whereas the propanone carbon retains two methyl groups. Hence



This is 2-methylbut-2-ene. Its formula is C_5H_{10} , and the identification is checked directly by reductive ozonolysis:



Step 5: Conclusion (i) Ethanal gives but-2-en-1-al by aldol condensation followed by heating; propanoic acid gives 2-chloropropanoic acid by $\text{Cl}_2/\text{red P}$ followed by hydrolysis. (ii) A is 2-methylbut-2-ene, B is ethanal and C is propanone.

Quick Tip to Solve: Identify the aldehyde from the intersection of Fehling and iodoform tests first; then use the five-carbon total to fix the ketone before reconnecting the carbonyl carbons.

34(b). (i) Distinguish with a suitable chemical test:

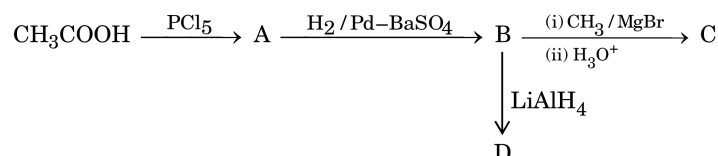
(1) $\text{CH}_3\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$

(2) Ethanal and Ethanoic acid

(ii) Write the structure of oxime of acetone.

(iii) Identify A to D in the following reaction scheme.

[5 marks]

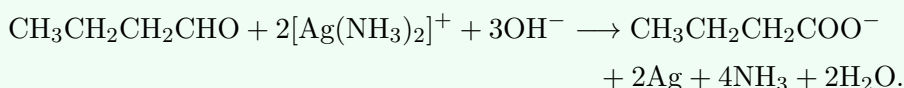


Solution:

Concept:

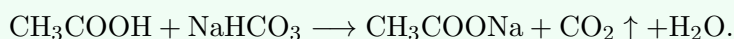
- Aldehydes reduce Tollens' reagent, ammoniacal silver nitrate, to metallic silver. Ordinary ketones do not give this test.
- Carboxylic acids liberate carbon dioxide from aqueous sodium hydrogen carbonate; neutral aldehydes do not.
- Hydroxylamine, NH_2OH , converts a carbonyl group $\text{C}=\text{O}$ into an oxime group $\text{C}=\text{N}-\text{OH}$.
- Rosenmund reduction converts an acid chloride to an aldehyde. A Grignard reagent adds its alkyl group to the carbonyl carbon, whereas LiAlH_4 reduces an aldehyde to a primary alcohol.

Step 1: (i)(1) Distinguish butan-2-one and butanal Add freshly prepared Tollens' reagent and warm gently in a water bath. Butanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$, gives a silver mirror because its aldehyde group is oxidised to a carboxylate ion and silver ions are reduced to silver. Butan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_3$, gives no silver mirror because it is a ketone.



Thus the presence or absence of a silver mirror distinguishes the two compounds without relying on their similar molecular formulae.

Step 2: (i)(2) Distinguish ethanal and ethanoic acid Add aqueous sodium hydrogen carbonate separately to the two samples. Ethanoic acid gives brisk effervescence of carbon dioxide:



Ethanal, CH_3CHO , gives no effervescence with this reagent. The gas from ethanoic acid turns limewater milky due to formation of CaCO_3 . This test detects the acidic carboxyl group and therefore clearly distinguishes it from the aldehyde group.

Step 3: (ii) Write acetone oxime Acetone reacts with hydroxylamine by condensation, eliminating water. Replace its carbonyl oxygen by $\text{N}-\text{OH}$, keeping both methyl groups attached to the same

Quick Tip to Solve: Track carbon count at B: methylmagnesium bromide adds one carbon to give propan-2-ol, while LiAlH_4 retains two carbons and gives ethanol.

carbon:

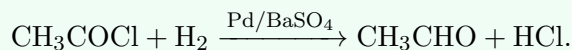


The oxime has the structural formula $(\text{CH}_3)_2\text{C}=\text{N}-\text{OH}$; the hydrogen of the hydroxyl group is bonded to oxygen.

Step 4: (iii) Identify A and B Phosphorus pentachloride replaces the acid's hydroxyl group by chlorine, forming ethanoyl chloride:

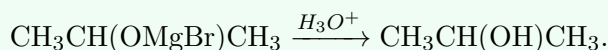


Therefore A is CH_3COCl . Hydrogen over palladium supported on barium sulfate then gives Rosenmund reduction:

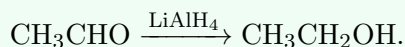


Thus B is ethanal, CH_3CHO . The poisoned catalyst limits reduction to the aldehyde stage.

Step 5: (iii) Identify C and D from the two branches In the upper branch, methylmagnesium bromide adds a methyl group to the carbonyl carbon of ethanal. Acidic hydrolysis converts the magnesium alkoxide to an alcohol:



Therefore C is propan-2-ol, a secondary alcohol with three carbon atoms. In the downward branch, LiAlH_4 reduces ethanal's carbonyl group without increasing the carbon count:



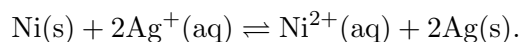
Hence D is ethanol, a primary alcohol. The upper and downward branches are independent reactions of B.

Step 6: Conclusion (i) Tollens' reagent gives a silver mirror with butanal but not butan-2-one; NaHCO_3 gives CO_2 effervescence with ethanoic acid but not ethanal. (ii) Acetone oxime is $(\text{CH}_3)_2\text{C}=\text{N}-\text{OH}$. (iii) A: CH_3COCl ; B: CH_3CHO ; C: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$; D: $\text{CH}_3\text{CH}_2\text{OH}$.

Quick Tip to Solve: Track carbon count at B: methylmagnesium bromide adds one carbon to give propan-2-ol, while LiAlH_4 retains two carbons and gives ethanol.

35(a). (i) State Kohlrausch's law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.

(ii) Calculate the maximum work and $\log K_c$ for the given reaction at 298 K:



Given: $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$, $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$; $1F = 96500 \text{ C mol}^{-1}$.

[5 marks]

Solution:

Concept:

- At infinite dilution, each ion contributes independently to the limiting molar conductivity: $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where ν is the number of each ion per formula unit and λ° is its limiting ionic molar conductivity.
- For standard reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per reaction as written.
- The equilibrium relation is $\Delta_r G^\circ = -2.303RT \log K_c$, so $\log K_c = nFE^\circ_{\text{cell}}/(2.303RT)$; here $\log$ denotes the common logarithm.

Step 1: (i) State the law and apply it to acetic acid Kohlrausch's law states that at infinite dilution, each ion makes a definite contribution to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. Thus the limiting molar conductivity is the sum of the individual ionic contributions, with their stoichiometric coefficients. Acetic acid gives one hydrogen ion and one acetate ion per molecule, hence

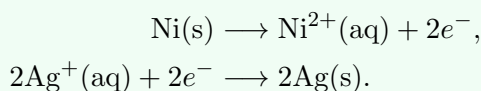
$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-).$$

It can also be obtained from strong electrolytes:

$$\begin{aligned}\Lambda_m^\circ(\text{CH}_3\text{COOH}) &= \Lambda_m^\circ(\text{HCl}) \\ &+ \Lambda_m^\circ(\text{CH}_3\text{COONa}) - \Lambda_m^\circ(\text{NaCl}).\end{aligned}$$

Adding these ionic contributions cancels Na^+ and Cl^- , leaving exactly the hydrogen and acetate contributions.

Step 2: (ii) Identify the electrodes and calculate the standard emf Nickel is oxidised at the anode and silver ions are reduced at the cathode:



Therefore $n = 2$; the coefficient of silver does not multiply its electrode potential. Using both given values as reduction potentials,

$$E^\circ_{\text{cell}} = 0.80 - (-0.25) = 1.05 \text{ V}.$$

Step 3: Calculate the maximum obtainable electrical work With standard electrode potentials, the

Quick Tip to Solve: Count the two transferred electrons first, then subtract the nickel reduction potential with its negative sign; never multiply an electrode potential by a stoichiometric coefficient.

corresponding standard free-energy change is

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(1.05) \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

For reversible operation, the maximum electrical work delivered by the cell is the magnitude $-\Delta_r G^\circ$. Thus the cell can deliver 202.65 kJ for one mole of the reaction as written. With the convention that work done on the system is negative for a delivering cell, its electrical work is $-202.65 \text{ kJ mol}^{-1}$.

Step 4: Calculate the equilibrium constant logarithm Using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T = 298 \text{ K}$,

$$\begin{aligned}\log K_c &= \frac{nFE_{\text{cell}}^\circ}{2.303RT} \\ &= \frac{2(96500)(1.05)}{2.303(8.314)(298)} \\ &\approx 35.52.\end{aligned}$$

Equivalently, using the usual rounded factor 0.0591 V at 298 K, $\log K_c = 2(1.05)/0.0591 \approx 35.53$. Both roundings show that equilibrium strongly favours the products.

Step 5: Conclusion $\Delta_m^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-)$. The maximum work obtainable is $202.65 \text{ kJ mol}^{-1}$ of reaction, with $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$, and $\log K_c \approx 35.5$.

Quick Tip to Solve: Count the two transferred electrons first, then subtract the nickel reduction potential with its negative sign; never multiply an electrode potential by a stoichiometric coefficient.

OR

35(b). (i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu^{2+} to Cu?

(ii) Calculate emf of the following cell at 298 K for



$[E^\circ_{\text{cell}} = +2.71 \text{ V}, 1 \text{ F} = 96500 \text{ C mol}^{-1}, \log 10 = 1]$

[5 marks]

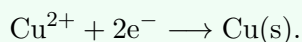
Solution:

Concept:

- Faraday's first law states that the mass m of a substance deposited or liberated at an electrode is directly proportional to the charge q passed through the electrolyte: $m = Zq = ZIt$, where Z is the electrochemical equivalent, I is current and t is time.
- One Faraday is the charge carried by one mole of electrons: $F = 96500 \text{ C mol}^{-1}$. The required number of moles of electrons follows from the balanced electrode reaction.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Quick Tip to Solve: Write the balanced cell reaction first: its electron count gives n , and its aqueous products divided by reactants give Q .

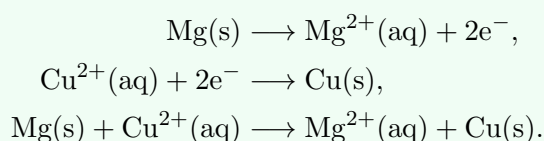
Step 1: (i) State the law and balance the copper reduction The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus, for a given electrolyte, $m \propto q$, or $m = ZIt$. This means that doubling the charge doubles the deposited mass, provided the same electrode reaction occurs. Copper(II) ions undergo the reduction



Each copper ion accepts two electrons, so reduction of one mole of copper(II) ions consumes two moles of electrons. The charge calculation is

$$q = (2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) = 193000 \text{ C}.$$

Step 2: (ii) Identify the cell reaction and reaction quotient Magnesium is oxidised at the left-hand electrode, while copper(II) is reduced at the right-hand electrode. The half-reactions and their sum are



Consequently $n = 2$. Magnesium ions are products and copper(II) ions are reactants. Omitting the pure solids from the quotient gives

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.1}{0.01} = 10.$$

Step 3: Substitute into the Nernst equation Using the given standard emf and $\log 10 = 1$,

$$\begin{aligned}E_{\text{cell}} &= 2.71 - \frac{0.0591}{2} \log 10 \\ &= 2.71 - 0.02955 \\ &= 2.68045 \text{ V}.\end{aligned}$$

Since $Q > 1$, the logarithmic correction is positive and is subtracted from the standard emf. The calculated emf is therefore slightly smaller than 2.71 V, consistent with the product-to-reactant concentration ratio.

Step 4: Conclusion (i) Faraday's first law is $m = ZIt$; reduction of 1 mol of Cu^{2+} requires $2 \text{ F} = 1.93 \times 10^5 \text{ C}$. (ii) The emf of the given cell at 298 K is $E_{\text{cell}} \approx 2.68 \text{ V}$.

Quick Tip to Solve: Write the balanced cell reaction first: its electron count gives n , and its aqueous products divided by reactants give Q .